Ch. 6 Electronic Structure and The Periodic Table

6-1: Light, Photon Energies, and Atomic Spectra

1. The Wave Nature of Light: Wavelength and Frequency
2. The particle Nature of Light; Photon Energies
3. Atomic Spectra

6-2: The Hydrogen Atom 氫原子模型

1. Bohr Model
2. Quantum Mechanical Model

6-3: Quantum Number 量子數

1. First Quantum Number, n; Principal Energy Levels
2. Second Quantum Number, l; Sublevels（s, P,d,f）
3. Third Quantum Number, m_l; Orbitals
4. Fourth Quantum Number, M_s: Electron Spin
5. Pauli Exclusion Principle

6-4: Atomic Orbitals; Shapes and Size

6-5: Electron Configurations in Atoms

1. Electron Configuration from Sublevel Energies
2. Filling of Sublevels and the Periodic Table
3. Electron Configuration from the periodic Table

6-6: Orbital Diagrams of Atoms

6-7: Electron Arrangements in Monatomic Ions

1. Ions with Noble-Gas Structures
2. Transition Metal Cations

6-8: Periodic Trends in the Properties of Atoms

1. Atomic Radius
2. Ionic Radius
3. Ionization Energy
4. Electronegativity

Ch. 6 Electronic Structure and The Periodic Table

Ch 2. 原子構造: 原子核：中子 + 質子
外圍： 電子
Ch 6. 電子的結構
╰→ energy levels, orbitals.

§ 6-1 Light, Photon energies, and Atomic Spectra

§ The wave nature of light： wavelength (l) and frequency(n)
Light travels trough space as a wave. Waves have three primary characteristics.

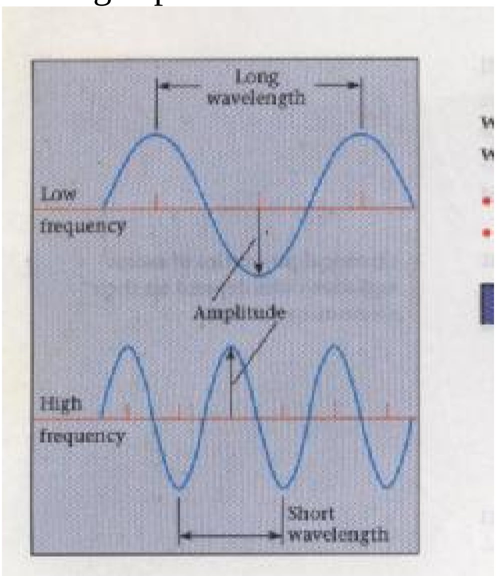

Fig 6.1: Characteristics of waves.

(1) Wavelength l : The distance between two consecutive crests or troughs. (nm)
(2) Frequency n : The number of wave cycles that pass a given point in unit time. (s^{-1}; Hz)
(3). Amplitude y : The height of a crest or the depth of a trough.
╰→ 唸 “psi”

$$l n = c$$

c : the speed of light in a vacuum $2.998 \times 10^{8}\ {}^{m}\!/\!_{s}$

Ex 6.1: You sit in your back yard on a warm summer evening watching the red sky (λ = 625 nm) at sunset and listening to music from your CD player. The laser in the latter has frequency 3.84 x 10^{14} s^{-1}.
(a) What is the frequency of the radiation from the red sky？
(b) What is the wave length of the laser in nm？

Ans:

(a) $l n = c$

$$n = \frac{c}{l}\ ; \qquad l = 625\ \text{nm} = 625\times10^{-9}\ \text{m} = 6.25\times10^{-7}\ \text{m}$$

$$= \frac{2.998\times10^{8}\ m/s}{6.25\times10^{-7}\ \text{m}}$$

$$= 4.80\times10^{14}\ \text{s}^{-1} = 4.80\times10^{14}\ \text{Hz}$$

(b) $$l = \frac{c}{n}$$

$$= \frac{2.998\times10^{8}\ m/s}{3.84\times10^{14}\ \text{s}^{-1}}$$

$$= 7.81\times10^{-7}\ \text{m} = 781\ \text{nm}$$

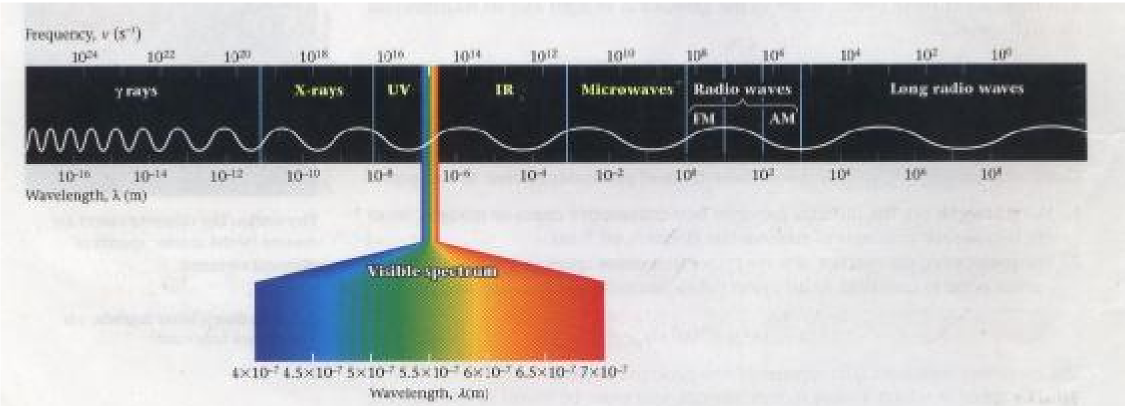

FIGURE 6.2
The electromagnetic spectrum. Note that only a small fraction is visible to the human eye. OHT

Fig 6.2：The electromagnetic spectrum.

Visible light

紫外線 uv　|← 400 ~ 700 nm →|　紅外線 IR

(ultraviolet)　紫　←　紅　(infrared)

§ The particle nature of light, photon energies

1900 – 1910：

Max Planck：blackbody radiation

Albert Einstein：photo electric effect

⇓

Light generates a stream of particles called photons, whose energy is given as:

$$E = h n = \frac{hC}{l}$$

h：Planck's constant　$6.626\times10^{-34}\ J\cdot s$

Ex 6.2: Sodium vapor lamp are commonly used to illuminate highways because of their intense yellow-orange emissions at 589 nm.

(a) Calculate the energy, in joules, of one photon of this light.

(b) Calculate the energy, in kilojoules, of one mole of such photons.
(c) To sense visible light, the optic never needs at least 2.0×10^{-17} J of energy to trigger impulses that reach the brain. How many photons of the sodium lamp emissions are needed to “see” the yellow light？

Ans：

$$(a)\ \ E = \frac{hC}{l} = \frac{(6.626\times10^{-34})\times(2.998\times10^{8})}{5.89\times10^{-7}} = 3.37\times10^{-19}\ \text{J}$$

$$(b)\ \ \text{E} = \frac{3.37\times10^{-19}\ \text{J}}{1\ \text{photon}} \times \frac{1\ \text{kJ}}{1000\ \text{J}} \times \frac{6.022\times10^{23}\ \text{photons}}{1\ \text{mol}} \qquad \text{J}$$

$$= 203\ \text{kJ}$$

$$(c)\ \ \text{n} = \frac{2.0\times10^{-17}\ \text{J}}{3.37\times10^{-19}\ \ J/photon} = 59\ \text{photons}$$

§ Atomic Spectra

Isaac Newton:

The visible light from the sun can be broken down into its various color components by a prism. The spectrum obtained is continuous. 400 ~ 700 nm

High energy of gaseous elements:

The spectrum consist of discrete lines given off at specific wavelengths.

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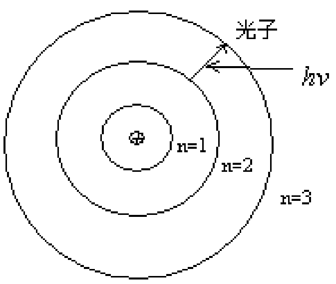
每一元素(氣態)均有特定光譜，可用以鑑定其種類.

Na： 589.0 nm and 589.6 nm (黃光)

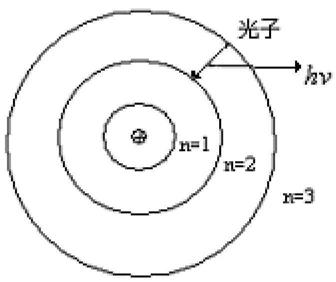
└→ 用途：高速公路 Na 蒸氣燈

$$E = hn = \frac{hC}{l}$$

Photons are produced when an electron moves from one energy level to another.



低能階 → 高能階；吸收能量 E “ – “

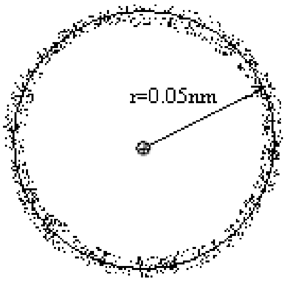


高能階 → 低能階；釋放能量 E ” + “

§ 6-2 The hydrogen atom

1913 Niels Bohr (1922 Nobel Prize in physics)

Bohr model：



Bohr's equation：

$$E_n = -\frac{R_H}{n^2}$$

E_n ： energy of electron; J.

R_H : Rydberg constant = 2.180×10^{-18} J

n: principal quantum number

1. Zero energy:
   The proton and electron are completely separated. 即 n = ∞

   $E_\infty = 0$ ∴ E_n 値 " – "
2. n =1 ground state, 其餘 n > 1 爲 excited state.

3. When an excited electron gives off energy as a photon of light, it drops back to a lower energy state.

$$n_1 \to n_2 : \Delta E = -R_H\left(\frac{1}{n_1{}^2} - \frac{1}{n_2{}^2}\right)$$

$$h\nu = -R_H\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right]$$

$$\nu = \frac{R_H}{h}\left[\frac{1}{n_2^2} - \frac{1}{n_1^2}\right]$$

$R_H = 2.180\times10^{-18}$ J

$h = 6.626\times10^{-34}$ J·S

$R_H/h = 3.290\times10^{15}$ Hz

Table 6.1: 由 $n_{hi} \to n_{lo}$ 釋出能量，放出光子

$n_{lo} = 1$	Lyman series; **uv**
$n_{lo} = 2$	Balmer series; **visible light**
$n_{lo} = 3$	Paschen series; **IR**
$n_{lo} = 4$	Brackett
$n_{lo} = 5$	Pfund

Ex 6-3：Calculate the wavelength in nanometers of the line in the Balmer series that results from the transition $n_1 = 4 \rightarrow n_2 = 2$.

Ans:

$$\Delta E = -R_H \left[\frac{1}{n_1^2} - \frac{1}{n_2^2} \right]$$

$$= -2.180 \times 10^{-18} \times \left[\frac{1}{4^2} - \frac{1}{2^2} \right]$$

$$= 4.088 \times 10^{-19} \text{ J}$$

$$\Delta E = hn = \frac{hC}{l}$$

$$4.088 \times 10^{-19} \text{ J} = 6.626 \times 10^{-34} \times \frac{2.998 \times 10^8}{l}$$

$$l = 4.859 \times 10^{-7} \; m = 485.9 \; nm$$

or

$$v = \frac{R_H}{h} \left[\frac{1}{n_2^2} - \frac{1}{n_1^2} \right]$$

$$= 3.290 \times 10^{15} \times \left[\frac{1}{2^2} - \frac{1}{4^2} \right] = 6.169 \times 10^{14} \; Hz$$

$$l = C/v = \frac{2.998 \times 10^8}{6.169 \times 10^{14}} = 4.860 \times 10^{-7} \; m = 486.0 \; nm$$

§ Quantum mechanical model 量子力學模型

Bohr hydrogen model: Highly successful only 0.1 % error. Apply on helium: 5 % error, 不適用

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An electron moving about the nucleus in a well-defined orbit at a fixed distance from the nucles had to be abandoned.

1924 法國人. Louis de Broglie 提出：

If light could show the behavior of particles (photons) as well as wave, then perhaps an electron which Bohr had treated as a particle, could behave like a wave.

⇓

wave mechanics 波動力學

⇓

quantum mechanics 量子力學

Quantum mechanics 與 Bohr hydrogen model 不同處：

1. The kinetic energy of an electron is inversely related to the volume of the region

to which it is confined.

⇒ 電子接近原子核時 electrostatic energy decreases 趨於安定
則電子可能全掉入原子核內，但實際並非如此，因爲同時會發生
動能上升，造成彼此牽制 ⇒當達平衡時原子最穩定

2. It is impossible to specify the precise position of an electron in an atom at a given instant.
唯一可行的是估計在特定區域內，電子出現的機率.

1826 Erwin Schrodinger
Wave properties of an electron in an atom

$$\frac{d^2y}{dx^2}+\frac{8p^2m(E-v)}{h^2}y=0$$

y ： amplitude
└→ wave function

y^2 is directly proportional to the probability of finding the electron at a particular point.

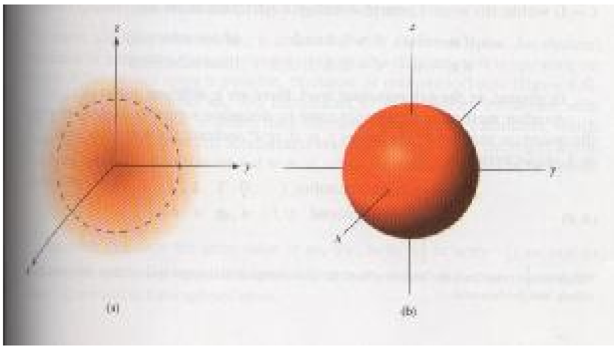

Fig 6.4 ：The electron distribution in the ground state of hydrogen atom.

顏色愈深，發現電子之機率愈大

§ 6-3 Quantum numbers

y 與 quantum numbers 相關聯
⇓
n , $\mathbf{l}$, $m_{\mathbf{l}}$, m_s
energy of the orbit; shape; orientation in space; electron spin direction

Each electron in an atom has a set of four quantum numbers： n , $\mathbf{l}$, $m_{\mathbf{l}}$, m_s .

§ First quantum number, n, principal quantum number 主量子數; principal energy levels 主能階

It represents the main energy levels for the electron or shells, and can be thought of a shell in the space where the probability of finding an electron with a particular value n is high.

n=1.2.3.4.5.6.7. n↑ energy level↑.

n, determine the energy of an electron.

n↑電子之能量↑

n 為正整數 1, 2, 3, 4, 5, 6, 7… (目前至 7)

§ Second quantum number, **l**, angular quantum number 角量子數⇒ sublevels (s, p, d, f, g, h…) 軌域

This quantum number specifies subenergy levels within the main energy levels (sub-shell) where the probability of finding an electron is high if that energy level is occupied.

Each principal energy level includes one or more sublevels.

⇓

符號：**l**

The general shape of the electron, larger values of **l** produce more complex shape.

例 n = 4 **l** = 0, 1, 2, 3 (n – 1) four sublevels.

∴ nth principal level, there are n different sublevels.

Type of sublevel s p d f

TABLE 6.2 Sublevel Designations for the First Four Principal Levels OHT

n	1	2		3			4			
ℓ	0	0	1	0	1	2	0	1	2	3
Sublevel	1s	2s	2p	3s	3p	3d	4s	4p	4d	4f

能量：

ns < np < nd < nf

§ Third quantum number, m_l, magnetic quantum number 磁量子數 ⇒ orbitals 副軌域

Each sublevel contains one or more orbitals, which differ from one another in the value assigned to the third quantum number, m_l. Determine the direction in space of the electron cloud surrounding the nucles. ⇒ 次軌域、副軌域

m_l = -**l**,…,-1,0,1,…,**l** 共(2**l**+1)個 orbitals

n = 4, ℓ = 0, 1, 2, 3

ℓ = 0	m_ℓ = 0	1 orbital — s
ℓ = 1	m_ℓ = -1, 0, 1	3 orbitals — p
ℓ = 2	m_ℓ = -2, -1, 0, 1, 2	5 orbitals — d
ℓ = 3	m_ℓ = -3, -2, -1, 0, 1, 2, 3	7 orbitals — f

∴ s 有一個副軌域，p 有三個副軌域
d 有五個副軌域，f 有七個副軌域

§ Fourth quantum number, m_s, electron spin quantum number.

Associated with electron spin, clockwise and counterclockwise

$$m_s = +\frac{1}{2} \qquad m_s = -\frac{1}{2}$$

TABLE 6.3 Permissible Values of the Quantum Numbers Through n = 4

n	ℓ	m_ℓ	m_s
1	0 (1s)	0	$+\frac{1}{2}, -\frac{1}{2}$
2	0 (2s)	0	$+\frac{1}{2}, -\frac{1}{2}$
	1 (2p)	−1, 0, +1	$\pm\frac{1}{2}$ for each value of m_ℓ
3	0 (3s)	0	$+\frac{1}{2}, -\frac{1}{2}$
	1 (3p)	−1, 0, +1	$\pm\frac{1}{2}$ for each value of m_ℓ
	2 (3d)	−2, −1, 0, +1, +2	$\pm\frac{1}{2}$ for each value of m_ℓ
4	0 (4s)	0	$+\frac{1}{2}, -\frac{1}{2}$
	1 (4p)	−1, 0, +1	$\pm\frac{1}{2}$ for each value of m_ℓ
	2 (4d)	−2, −1, 0, +1, +2	$\pm\frac{1}{2}$ for each value of m_ℓ
	3 (4f)	−3, −2, −1, 0, +1, +2, +3	$\pm\frac{1}{2}$ for each value of m_ℓ

§ Pauli exclusion principle 包立不相容定理

No two electrons in an atom can have the same set of four quantum numbers.

Ex 6-4: Consider the following sets of quantum numbers (n, ℓ, m_ℓ, m_s). Which ones could not occur？For the valid sets identify the orbital involved.

Ans: a) 3, 1, 0, $+\frac{1}{2}$ 3p

b) 1, 1, 0, $-\frac{1}{2}$ ℓ = 0, …,(n – 1), ∵ n = 1, ℓ = 0 ∴ 不存在

c) 2, 0, 0, $+\frac{1}{2}$ 2s

d) 4, 3, 2, $+\frac{1}{2}$ 4f

e) 2, 1, 0, 0 $m_s = +\frac{1}{2}$ or $-\frac{1}{2}$ ∴ 不存在

Ex 6.5: (a) What is the capacity for electrons of an s sublevel？A p sublevel？A d sublevel？A f sublevel?

(b) What is the total capacity for electrons of the fourth principal level?

Ans:

a). s 軌域 $\mathbf{l} = 0$ $m_l = 0$ $m_s = +\frac{1}{2}$ or $-\frac{1}{2}$ $1 \times 2 = 2$ 個電子

p 軌域 $\mathbf{l} = 1$ $m_l = -1, 0, +1$ $m_s = +\frac{1}{2}$ or $-\frac{1}{2}$ $3 \times 2 = 6$ 個電子

d 軌域 $\mathbf{l} = 2$ $m_l = -2, -1, 0, +1, +2$ $m_s = +\frac{1}{2}$ or $-\frac{1}{2}$ $5 \times 2 = 10$ 個電子

f 軌域 $\mathbf{l} = 3$ $m_l = -3, -2, -1, 0, +1, +2, +3$ $m_s = +\frac{1}{2}$ or $-\frac{1}{2}$ $7 \times 2 = 14$ 個電子

b). n = 4 $\mathbf{l} = 0$ s 軌域 含 2 個電子

$\mathbf{l} = 1$ p 軌域 含 6 個電子

$\mathbf{l} = 2$ d 軌域 含 10 個電子

$\mathbf{l} = 3$ f 軌域 含 14 個電子 共 32 個 $= 2n^2$ 個

⇒ ↑ § ⇓ →∴∵ ～ –↓“C-1” ↳ ⇒ ・ $\Delta G = 0$ ΔE ℃？ ↵